

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PCT

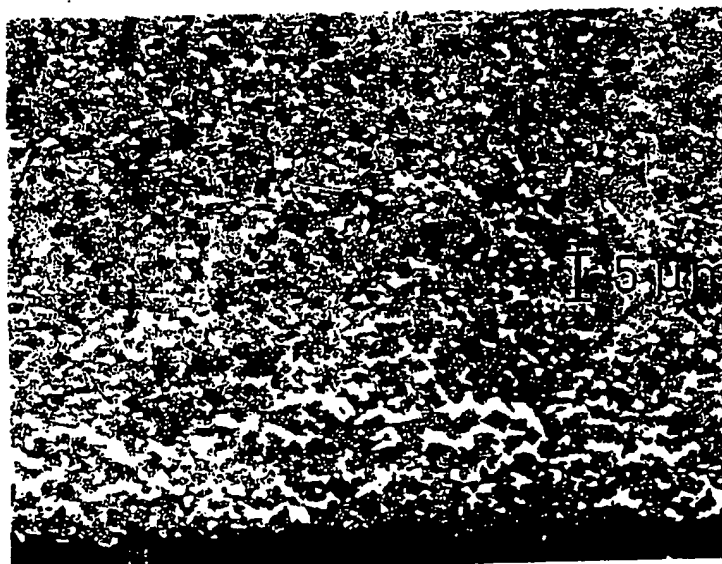
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C25F 3/02, 1/04, 3/22	A1	(11) International Publication Number: WO 92/20841 (43) International Publication Date: 26 November 1992 (26.11.92)
(21) International Application Number: PCT/SE92/00317 (22) International Filing Date: 14 May 1992 (14.05.92) (30) Priority data: 9101469-6 15 May 1991 (15.05.91) SE (71) Applicant: SANDVIK AB [SE/SE]; S-811 81 Sandviken (SE). (72) Inventor: SVENSSON, Rolf ; Sandalmakarbacken 9, S-126 39 Hägersten (SE). (74) Agents: TÅQUIST, Lennart et al.; Patent Department, Sandvik AB, S-811 81 Sandviken (SE).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), RU, SE (European patent). Published <i>With international search report.</i>

(54) Title: ETCHING PROCESS



(57) Abstract

The present invention relates to a method of removing by etching the binder phase from the surface of a hard material consisting of hard constituents in a binder phase based on cobalt and/or nickel. By carrying out the etching process electrolytically in

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	ML	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	RO	Romania
CA	Canada	IT	Italy	RU	Russian Federation
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TC	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		
ES	Spain				

Etching process

The present invention relates to an etching process for the purpose of removing the binder phase from the surface of cemented carbide inserts before applying coatings on said surface.

Coated cemented carbide inserts have now for many years been commercially available for chip cutting machining of metals in the metal cutting industry. Such inserts are commonly made of a metal carbide, normally WC, generally with addition of carbides of other metals such as Nb, Ti, Ta, etc and a metallic binder phase of cobalt. By depositing onto said inserts a thin layer of a wear resistant material such as TiC, TiN, Al₂O₃ etc separately or in combination it has been possible to increase the wear resistance at essentially maintained toughness. A still further improvement in properties has been obtained by subjecting the inserts to a binder phase enrichment in the surface below the coating, so called cobalt gradient. Binder phase enrichment can be accomplished, for instance, by sintering in vacuum with nitride addition as is disclosed in Swedish patent application 8201930-8 or by controlled cooling as disclosed in EP-A-337696. Such inserts, however, often also have a thin layer of binder phase on their surface and sometimes even with a layer of graphite thereon. The two latter layers have a negative effect on the process when carrying out CVD- or PVD-deposition, which results in layers with inferior properties and insufficient adherence. These layers must therefore be removed before carrying out the deposition process.

It is possible to remove such cobalt- and possible graphite-layers mechanically by blasting. The blasting method is, however, difficult to control. The difficulty resides in the inability to control consistently the

blasting depth with necessary accuracy, which leads to an increased scatter in the properties of the final product - the coated insert.

Chemical or electrolytic methods could be used as alternatives for mechanical methods. US Patent 4,282,289 discloses a method of etching in a gaseous phase by using HCl in an initial phase of the coating process. In EP-A-337 696 there is proposed a wet chemical method of etching in nitric acid, hydrochloric acid, hydrofluoric acid, sulphuric acid and similar or electro-chemical methods. From JP 88-060279 it is known to use an alkaline solution, NaOH, and from JP 88-060280 to use an acid solution. JP 88-053269 discloses etching in nitric acid prior to diamond deposition. There is one drawback with these methods, namely, that they are incapable of only removing the cobalt layer. They also result in deep penetration, particularly in areas close to the edge. The etching medium not only removes cobalt from the surface but also penetrates areas between the hard constituent grains and as a result an undesired porosity between layer and substrate is obtained at the same time as the cobalt layer may partly remain in other areas of the insert.

It is therefore an object of the present invention to provide an etching method which does not give a deep penetration effect.

In Fig 1 there is shown in 1200 x magnification the structure of a cross-section of a surface zone of a cemented carbide insert after being subjected to electrolytic etching according to prior art and Fig 2 shows the structure after electrolytic etching according to the invention.

It has now surprisingly been found that electrolytic etching in a mixture containing concentrated sulphuric acid, H_2SO_4 , and concentrated phosphoric acid, H_3PO_4 ,

gives the desired effect of cleanly and effectively removing the surface layer of binder metal and any graphite. By using such a mixture of acids the cobalt layer on the surface will be effectively removed whereas the
5 cobalt in the channels between the hard constituent grains will not be etched away. The binder phase layers between the carbide grains, which are necessary for the strength of the cemented carbide are not affected. The method is even self-regulating. When the cobalt layer
10 has disappeared the process stops which means that the length of the process time is not critical.

The reason why the electrolyte according to the invention gives rise to such positive results is not completely known. It is probably due to the viscosity in
15 combination with the solubility of the salts formed. If, e.g., diluted sulphuric acid is used deep penetration is obtained.

The electrolytic etching process is carried out in a manner known per se. Voltage, current density, time etc
20 depend of the thickness of cobalt- and possible graphite layer, number of inserts, design of equipment and have to be found by experiment to obtain the best result. The electrolyte shall contain a mixture of commercially available concentrated sulphuric- and phosphoric acids
25 in volume ratio (0,5-2):1, preferably (0,75-1,25):1, most preferably (0,95-1,05):1. The water content of the solution shall be <50 %, preferably <25 %, most preferably <15 %. The etching is suitably carried out at a combination of time, current and exposed surface up to
30 150 As/cm². However, in production scale operating at constant voltage is generally more convenient. The temperature of the electrolyte shall be 25-60°C. Precautions must be adhered to when carrying out the etching since explosive or health damaging gases and vapours
35 might develop.

After finalizing the etching process, the inserts shall be neutralized and cleaned, for instance, by rinsing in alkaline baths followed by rinsing in water. Cleaning is suitably carried out by ultra-sonic means
5 followed by drying.

Still further improved results can be obtained in those cases where a graphite layer is present on top of the cobalt layer. By carrying out a light wet blasting or mechanical working before the etching process essentially only the graphite is removed. In this way those
10 problems are avoided that might occur when insufficient electrical contact is obtained between inserts and current supply which leads to insufficient etching effect. In addition, difficulties with removal of graphite flakes during the etching process are avoided.
15

Removing the binder phase by the method of this invention results in a substrate with a well defined hard surface, which can be used uncoated, but is very suitable for the deposition of a thin wear-resistant layer of
20 a metal carbide, oxide, nitride or mixtures thereof, e.g., TiC, TiN, Al₂O₃, diamond etc. by CVD- and PVD-methods. A further advantage of using the present method is the reduced risk for decarburization of the substrate surface and eta phase formation associated therewith
25 when carrying out deposition with CVD-methods. The decarburized zone in certain cases gives negative effects on the cutting properties of the final product.

The invention has been described above with reference to binder phase enriched cemented carbide. The
30 method can also be applied to coated or uncoated conventional cemented carbide, i.e., hard material based on carbides of W, Ti, Ta and/or Nb in a binder phase of cobalt as well as to other types of hard materials containing hard constituents (carbides, nitrides, carbonitrides etc) in a binder phase based on cobalt and/or
35

nickel, such as titanium based carbonitride alloys usually called cermets.

Example 1 (prior art)

5 Cemented carbide inserts of type CNMG120408-QM with a composition of in addition to WC, 5,5 % Co, 8,5 % TiC + TaC + NbC and sintered in such a way that they had a cobalt enrichment in the surface zone and with a cobalt layer of about 2 μm thickness and a graphite layer of
10 about 2 μm thereon were subjected to electrolytic etching in diluted 10 % sulphuric acid. By applying 1-2 V voltage and 30-70 As/cm² weight losses of 55-130 mg/insert were obtained which resulted in etching away not only of cobalt from the surface but also in certain
15 areas up to 30 μm in depth, Fig 1.

Example 2

Cemented carbide inserts according to Example 1 were subjected to etching in a mixture of concentrated
20 sulphuric acid and concentrated phosphoric acid in a volume ratio of 1:1 at a temperature of about 50°C. In this case a weight loss of 10-14 mg/insert was obtained at an applied voltage 4,5-5 V and 100-140 As/cm² after the same time as in Example 1. The cobalt layer was re-
25 moved from the surface without any deep penetration as is evident from Fig 2.

Example 3

Example 2 was repeated with the difference that the
30 inserts were initially subjected to a light wet blasting with 150 mesh Al₂O₃ at 1.2 bar pressure during 2 min in order to remove the graphite layer. At 35-40 As/cm² and 6 V a weight loss of about 5-8 mg/insert without any deep etching was obtained.

Example 4

Example 2 was repeated with the difference that the etching was performed with an applied constant voltage of 15 V and 50-100 As/cm². The weight loss was in this case 10-12 mg/insert without any deep etching.

Example 5

Inserts of type TNMG160408-QF of a titanium based carbonitride alloy with a binder phase of about 10 % cobalt and 5 % nickel which after the sintering had a binder phase layer of about 2 μ m thickness on the surface were etched according to Example 2 but at 50-90 As/cm² and 6 V. The weight loss was 6-9 mg/insert. No deep penetration was observed.

Claims

1. A method of removing by etching the binder phase from the surface of hard material containing hard constituents in a binder phase based on cobalt and/or
5 nickel, c h a r a c t e r i z e d in that the etching is carried out electrolytically in a mixture comprising concentrated sulphuric acid and concentrated phosphoric acid in the volume ratio of (0,5-2):1 with a water content of <50 % at a temperature of 25-60°C.
- 10 2. A method as defined in claim 1, c h a r a c t e r i z e d in that the material is initially subjected to a light blasting or other mechanical treatment before carrying out the electrolytic etching.

1/1

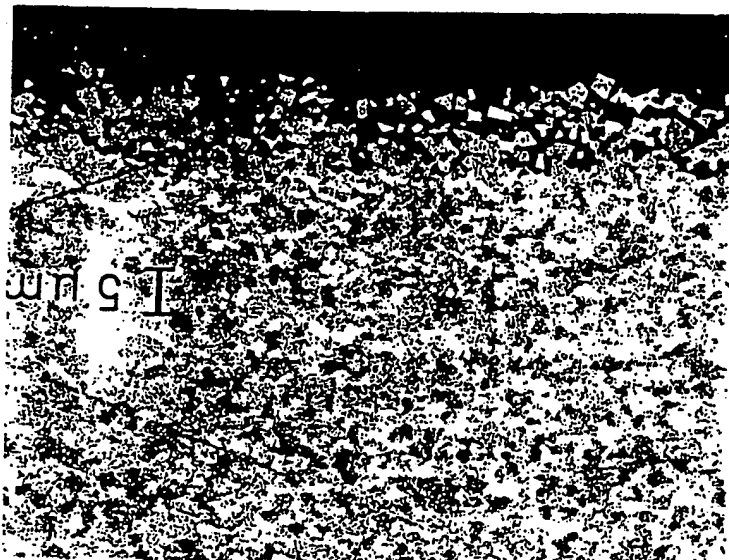


Fig 1

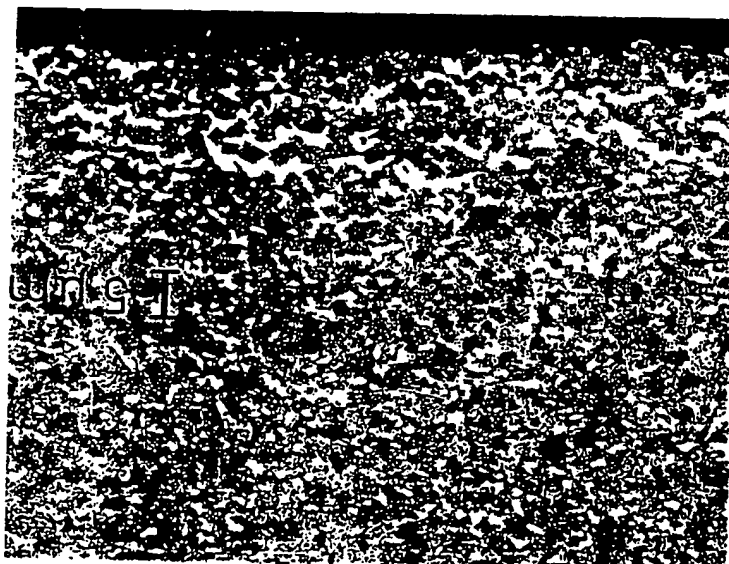


Fig 2

INTERNATIONAL SEARCH REPORT

International Application No **PCT/SE 92/00317**

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 25 F 3/02, 1/04, 3/22		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC5	C 25 F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched ⁸		
SE,DK,FI,NO classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category *	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP, A1, 0249650 (POLIGRAT GMBH) 23 December 1987, see column 2, line 14 - line 31; column 5, line 1 - line 12 --	1
X	US, A, 2334699 (CHARLES L. FAUST) 23 November 1943, see page 1, column 2, line 11 - line 21; page 2, column 2, line 42 - line 58; claim 1 --	1
X	US, A, 2820750 (PERCY ALLAN CHARLESWORTH) 21 January 1958, see column 1, line 42 - line 50; column 2, line 32 - line 43 --	1
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
15th July 1992	1992 -07- 30	
International Searching Authority	Signature of Authorized Officer	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	DE, A1, 2733304 (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.) 26 January 1978, see claims 1,3 -- -----	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/SE 92/00317**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 29/05/92. The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A1- 0249650	87-12-23	JP-A-	63004100	88-01-09
		US-A-	4740280	88-04-26
US-A- 2334699	43-11-23	BE-A-	478064	00-00-00
		CH-A-	271130	00-00-00
		LU-A-	28863	00-00-00
		NL-C-	71883	00-00-00
		US-A-	2338321	00-00-00
US-A- 2820750	58-01-21	NONE		
DE-A1- 2733304	78-01-26	FR-A-	2359195	78-02-17
		JP-C-	1004345	80-06-30
		JP-A-	53012740	78-02-04
		JP-B-	54040381	79-12-03
		US-A-	4169026	79-09-25